Kinetic Study of H+HF(v = 3): Kinetic Isotope Effect and Temperature Dependence
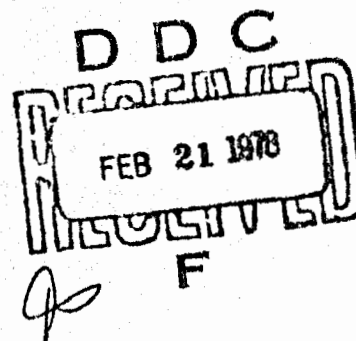
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Interim Report

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rates of HF(v = 3) removal by H and D atoms were measured between 200 and 295 K in a laser-induced fluorescence-discharge flow-tube apparatus. The removal rates by H atoms were found to increase from 1.3×10^{13} cm^3/mol-sec at 295 K to 4×10^{13} cm^3/mol-sec at 200 K. The removal of HF(v = 3) by D atoms is somewhat slower, but the removal rates have a similar negative temperature dependence.

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

There are several mechanisms by which H atoms can remove $HF(v = 3)$, i.e., reaction to form $H_2 + F$ or deactivation to $HF(v = 0, 1,$ or $2)$ with or without exchange of the F atom. The several possibilities are discussed and compared to theoretical calculations.

PREFACE

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I. INTRODUCTION

The deactivation of vibrationally excited HF by the products of the F + H$_2$ reaction directly affects the performance of the HF chemical laser. The deactivation of HF(v) by H has been studied by both theoretical calculations[1,2] and experimental investigations.[3-6] The trajectory calculations of Thompson[1] and Wilkins[2] were the first indications that H atoms might be efficient deactivators of the upper levels of HF. Subsequently, in two experimental studies,[3,6] rate coefficients for HF(v = 3) deactivation were found that were greater than 10^{13} cm^3/mol-sec. There are several possible channels by which HF(v = 3) can be removed by H atoms; unfortunately, the trajectory calculations[1,2] can only be used as a rough guide since the *London-Eyring-Polanyi-Sato* (LEPS) potential energy surfaces used differ significantly from two recent quantum mechanical calculations of the H-F-H configuration.[7-9]

In a previous study,[6] we employed the laser-induced fluorescence technique to measure the room-temperature removal rate of HF(v = 3) and HF(v = 2) by H atoms. In the present study, the measurements were extended to 200 K [for HF(v = 3)], and the removal rate of HF(v = 3) by D was measured as a function of temperature. With a detailed analysis of these kinetic data and careful consideration of the F-H-H thermochemistry, the following conclusions were reached:

1. The reaction H + HF(v = 3) → H$_2$ + F contributes ~20% of the observed removal rate at 295 K. This channel must have a small positive activation energy.

2.   The dominant mechanism for HF(v = 3) removal has
      a negative temperature dependence, suggestive of com-
      plex formation, attractive interactions, or orbiting
      collisions.   The possible role of F-atom exchange is
      discussed.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The basic experimental apparatus has been previously described.[6] In the present experiments, the flow tube was immersed in a stirred low-temperature slush. A dry ice-ethanol mixture was used for the 200 K measurements, and a water-ethanol mixture was used for those at 240 K. Cold N_2 was slowly passed through Cu coils at the bottom of the bath to maintain the slush. The temperature of the slush agreed within ~ 1 to $2°C$ with the reading of a thermocouple mounted in the center of the flow tube downstream of the observation point. The HF$(v = 3)$ level was populated by sequential absorption of infrared laser photons from a multiband pulsed HF laser. This level was monitored by $3 \to 0$ overtone fluorescence at ~ 900 nm.[6] Hydrogen (or D) atoms were created by a microwave discharge in H_2(or D_2) and monitored by isothermal calorimetry.[5, 6]

Experiments were performed at total pressures of ~ 3 Torr with partial pressures of $\sim 1 \times 10^{-3}$ Torr HF, $\sim 3 \times 10^{-2}$ Torr H_2, and $\leqslant 2 \times 10^{-2}$ Torr H atoms; He made up the balance.

III. RESULTS

Within the precision of the data, the $3 \rightarrow 0$ laser-induced fluorescence traces could be characterized by single exponential decays for the first one to two decay times. The measured fluorescence traces were plotted on semi-log paper, and the exponential decay times τ were determined. In each experiment, the decay times were measured with the microwave discharge on τ_{on} and with the discharge off τ_{off} at the same flow rates. The measured decay times as well as the experimental conditions are listed in Tables I through III. The overall removal rate coefficient of HF(v = 3) is designated k and was calculated with the equation

$$\Delta(1/\tau) = k[H] \tag{1}$$

where $\Delta(1/\tau) = \tau_{on}^{-1} - \tau_{off}^{-1}$. The interpretation of this k requires discussion because there are several channels for HF(v = 3) removal.

The data obtained at several temperatures are plotted in Fig. 1. The removal rate of HF(v = 3) by H is faster at 200 than at 295 K. Although the temperature range is small and the scatter is somewhat large, the data imply an activation energy between 0 and -750 cal/mol. The removal rates by D atoms are ~10 to 20% smaller than those for H atoms at both 295 and 200 K. The stated uncertainty in the deduced rates (30%) reflects both systematic errors in the isothermal probe and flow-meter calibrations and experimental scatter in the data.

Table I. Removal Rate of HF(v = 3) by H Atoms at 240 K

Run	P_{total}, Torr	$[H] \times 10^{10}$, mol/cm^3	$[H_2] \times 10^9$, mol/cm^3	τ_{on}, μsec	τ_{off}, μsec	$\Delta(I/\tau) \times 10^{-4}$, sec^{-1}	T, °K	$k \times 10^{-13}$, cm^3/mol-sec
1	2.85	9.1	2.0	16.7	136	5.3	240	5.8
2	2.85	9.7	2.0	12.5	136	7.3	238	7.5
3	2.85	10.6	2.0	12.7	136	7.2	236	6.8
4	2.85	6.94	2.0	18.4	136	4.7	234	6.8
5	2.85	4.9	2.0	28.9	136	2.7	235	5.6
								6.5 Average

Table II. Removal Rate of HF(v = 3) by H Atoms at 200 K[a]

Run	P_{total}, Torr	$[H] \times 10^{10}$, mol/cm^3	$[H_2] \times 10^9$, mol/cm^3	τ_{on}, μsec	τ_{off}, μsec	$\Delta(1/\tau) \times 10^{-4}$, sec^{-1}	T, °K	$k \times 10^{-13}$, cm^3/mol-sec
1	2.95	7.2	1.5	13.8	186	6.7	200	9.3
2	2.95	7.2	1.5	13.8	186	6.7	200	9.3
3	2.95	6.2	1.2	17.1	186	5.3	200	8.5
4	2.95	6.4	1.2	17.6	186	5.1	202	8.0
5	2.95	8.8	1.5	11.2	186	8.4	200	<u>9.6</u>
								8.9 Average
1	2.9	7.4	1.5	11.8	150	7.8	200	11.0
2	2.9	7.0	1.5	11.4	130	8.0	200	11.0
3	2.9	5.7	1.2	12.7	130	7.1	200	13.0
4	2.9	5.4	1.2	12.5	130	7.2	200	13.0
5	2.9	6.4	1.3	13.7	130	6.5	200	<u>10.0</u>
								11.6 Average
1	2.95	11	2.2	10.1	177	9.3	200	8.6
2	2.95	6.6	1.5	13.5	177	6.8	200	10.4
3	2.95	6.7	1.5	14.5	177	6.3	200	9.5
4	2.95	5.4	1.5	15.3	177	6.0	200	<u>11.0</u>
								9.9 Average

[a]These data were taken on three separate days.

Table III. Removal Rate of HF(v = 3) by D Atoms at 295 and 200 K[a]

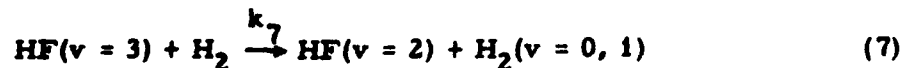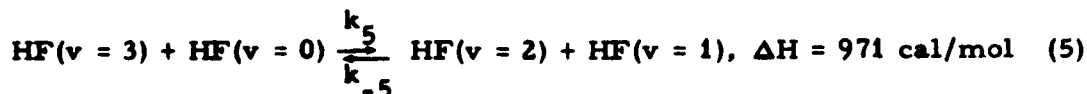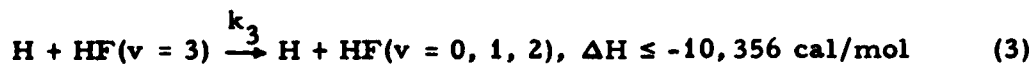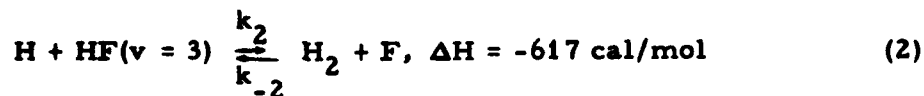| Run	P_{total}, Torr	$[D] \times 10^{10}$, mol/cm^3	$[D_2] \times 10^9$, mol/cm^3	τ_{on}, μsec	τ_{off}, μsec	$\Delta(1/\tau) \times 10^{-4}$, sec^{-1}	T, °K	$k \times 10^{-13}$, $cm^3/mol\text{-}sec$
1	2.85	8.1	3.2	17.0	146	5.2	295	6.4
2	2.85	9.0	3.2	14.5	146	6.2	295	6.9
3	2.85	8.6	3.2	15.8	146	5.7	295	6.6
4	2.85	9.5	3.2	15.8	143	5.6	295	5.9
5	2.90	8.1	3.2	18.5	132	4.7	295	5.8
6	2.90	7.8	3.2	19.0	132	4.4	295	5.6
7	2.90	6.0	3.2	27.0	132	3.0	295	5.0
8	2.90	3.6	3.2	38.0	132	1.9	295	<u>5.2</u>
								5.9 Average
9	2.90	8.5	3.8	13.7	75	6.0	200	7.0
10	2.90	6.0	1.9	14.8	105	5.8	200	9.7
11	2.90	6.4	1.9	18.3	105	4.5	200	<u>7.1</u>
								7.9 Average

[a]These data were taken on two separate days.
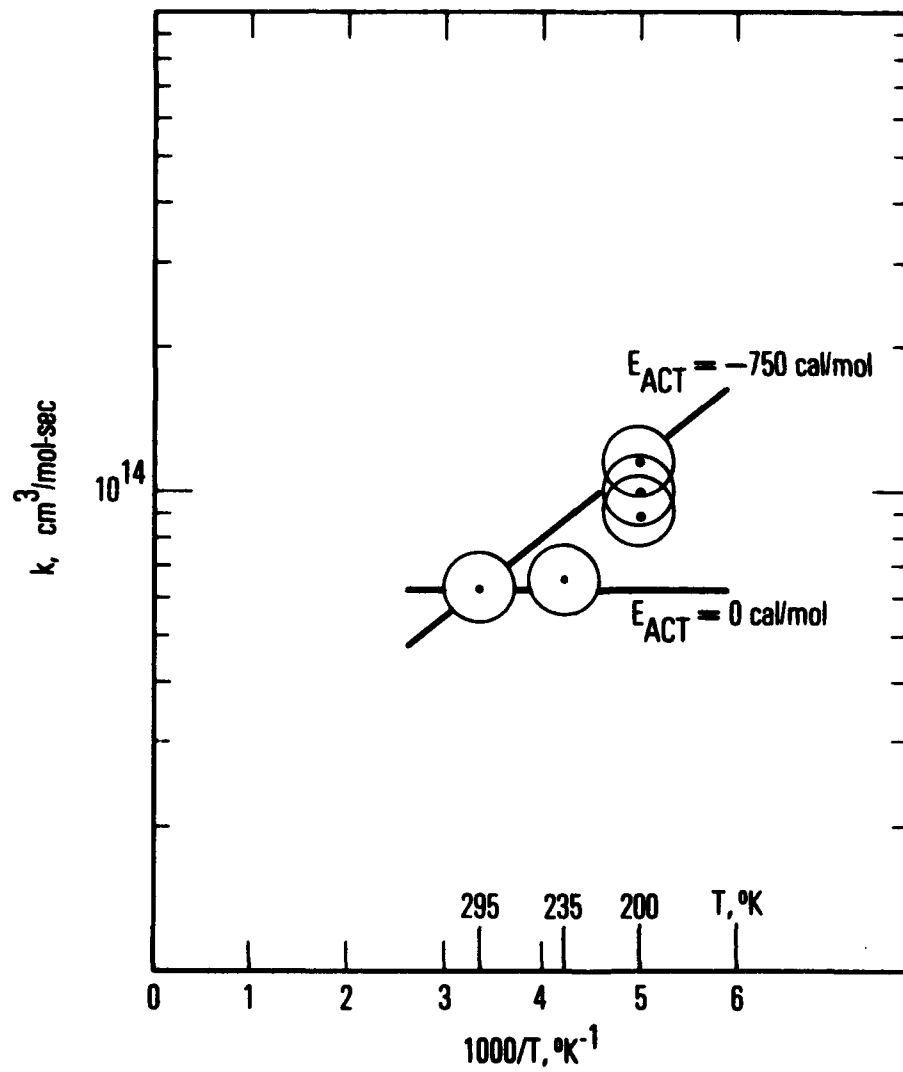
Fig. 1. Removal rate of HF(v = 3) by H atoms

IV. DISCUSSION

A. REMOVAL OF HF(v = 3) BY H ATOMS AT 295 K

The disappearance of HF(v = 3) can be described with the following kinetic scheme.

$$H + HF(v = 3) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + F, \quad \Delta H = -617 \text{ cal/mol} \qquad (2)$$

$$H + HF(v = 3) \overset{k_3}{\longrightarrow} H + HF(v = 0, 1, 2), \quad \Delta H \leq -10,356 \text{ cal/mol} \qquad (3)$$

$$F + H_2 \overset{k_4}{\longrightarrow} HF(v = 0, 1, 2) + H, \quad \Delta H \leq -9,736 \text{ cal/mol} \qquad (4)$$

$$HF(v = 3) + HF(v = 0) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HF(v = 2) + HF(v = 1), \quad \Delta H = 971 \text{ cal/mol} \qquad (5)$$

$$HF(v = 3) + HF \overset{k_6}{\longrightarrow} HF(v = 2) + HF, \quad \Delta H = -10,356 \text{ cal/mol} \qquad (6)$$

$$HF(v = 3) + H_2 \overset{k_7}{\longrightarrow} HF(v = 2) + H_2(v = 0, 1) \qquad (7)$$

The removal of HF(v = 3) can occur by Reaction (2), which in the backward direction is a channel of the $F + H_2$ overall reaction, or by the deactivation channel, Reaction (3). The latter may be either a nonreactive inelastic collision or a reactive collision in which the F atom is abstracted by the

incoming H atom. With no H atoms present, the decay rate of HF(v = 3) can be described by

$$\frac{d [HF(v = 3)]}{dt [HF(v = 3)]} = -(k_5 + k_6) [HF(v = 0)] + k_{-5} \frac{[HF(v = 2)] [HF(v = 1)]}{[HF(v = 3)]}$$

$$-k_7 [H_2] - R \tag{8}$$

where R represents convection and diffusion losses out of the observation volume as well as radiative decay. The fluorescence data analyzed in Tables I through III decreased monotonically, indicating that the right-hand-side positive (pumping) term was always smaller than the negative (removal) terms. The laser could be detuned or the [HF] raised so that this was not true, i.e., the fluorescence increased initially and then decayed. With the deactivation rates listed in Table IV and typical concentrations of HF $\sim 5 \times 10^{-11}$ and $H_2 \sim 1.5 \times 10^{-9}$ mol/cm^3, $(k_5 + k_6)$ [HF] $\sim 2 \times 10^3$ sec^{-1} and $k_7 [H_2] \sim 3 \times 10^2$ sec^{-1}. These rates and an estimate of R $\sim 2 \times 10^3$ sec^{-1} indicate a total decay rate of $\sim 4 \times 10^3$ sec^{-1} and a decay time of ~ 250 μsec, which are in reasonable agreement with the observed decay times at room temperature.

When the laser was tuned to maximize the HF(v = 3) fluorescence, the signal decayed exponentially for one to two decay times when no H atoms were present. At longer times, the decay rate decreased, probably because the pumping term k_{-5} becomes increasingly important at the smaller HF(v = 3) concentrations. Hydrogen[12] does not contribute greatly to the

Table IV. Reaction Rate Coefficients

Rate Coefficient	Assumed Value, cm^3/mol-sec	Reference
k_{-2}	4.2×10^{12}	10, see text
k_2	1.37×10^{13}	See text
$k_4 + k_{-2}$	1.5×10^{13}	10
$k_5 + k_6$	2.9×10^{13}	11
k_7	2.0×10^{11}	12

decay rate even though the $[H_2] \approx 30\ [HF]$; the back reaction, Reaction (-7), is insignificant compared with Reaction (-5).

When H atoms are present, two additional terms must be added to the right-hand side of Equation (8). They are

$$-(k_2 + k_3)\ [H] + k_{-2}\ \frac{[F]\ [H_2]}{[HF(v = 3)]} \tag{9}$$

The sum of these two terms has a large negative value, compared to the other terms in Equation (8), since the HF(v = 3) decayed typically five to ten times faster with the H atoms than without. Therefore, the disappearance rate of HF(v = 3) can be approximated by

$$\frac{d\ [HF(v = 3)]}{dt\ [HF(v = 3)]} = -(k_2 + k_3)\ [H] + k_{-2}\ \frac{[F]\ [H_2]}{[HF(v = 3)]}$$

$$- (k_5 + k_6)\ [HF(v = 0)] - k_7\ [H_2] - R \tag{10}$$

If the second term on the right-hand side of Equation (10) is small, the decay is essentially exponential. The change in decay rate produced by the H atoms can be described by

$$\Delta\left(\frac{1}{\tau}\right) = \left(k_2 + k_3 - \frac{1}{2}\ k_7\right)[H] \approx (k_2 + k_3)\ [H] \tag{11}$$

This change in decay rate, if evaluated at time equal to zero, is always given by Equation (11). However, if $k_2 \gg k_3$, the effect of the pumping term

in Equation (10) must be taken into account if the decay rates are evaluated at longer times.

It is shown in the Appendix that the preceding equations are equivalent to those describing the V-V and V-R, T relaxation of an initially excited molecular species by a chaperone molecular species. The concentration of HF(v = 3) can be described by the sum of two exponentially decaying terms.

$$[HF(v = 3)] = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) \tag{12}$$

The solution is given in the Appendix to a somewhat simplified set of reactions. The values of the two inverse decay times λ_1 and λ_2 normalized with the quantity $Q + N$ are plotted in Fig. 2. They were calculated for $[H_2] = 3 \times 10^{-9}$ mol/cm^3 with the rate coefficients of Table IV and three values of k_3. In summary, $Q = k_2[H]$, and N is the sum of all other deactivation (negative) terms in Equation (10). $Q + N$ is always the initial deactivation rate of HF(v = 3); the initial deactivation rate should not be confused with λ_1. F atoms are produced by Reaction (2) until an equilibrium is established with Reaction (4), which removes them. This equilibrium is established quickly when H_2 is large compared to H. Thereafter, HF(v = 3) decays with the rate of

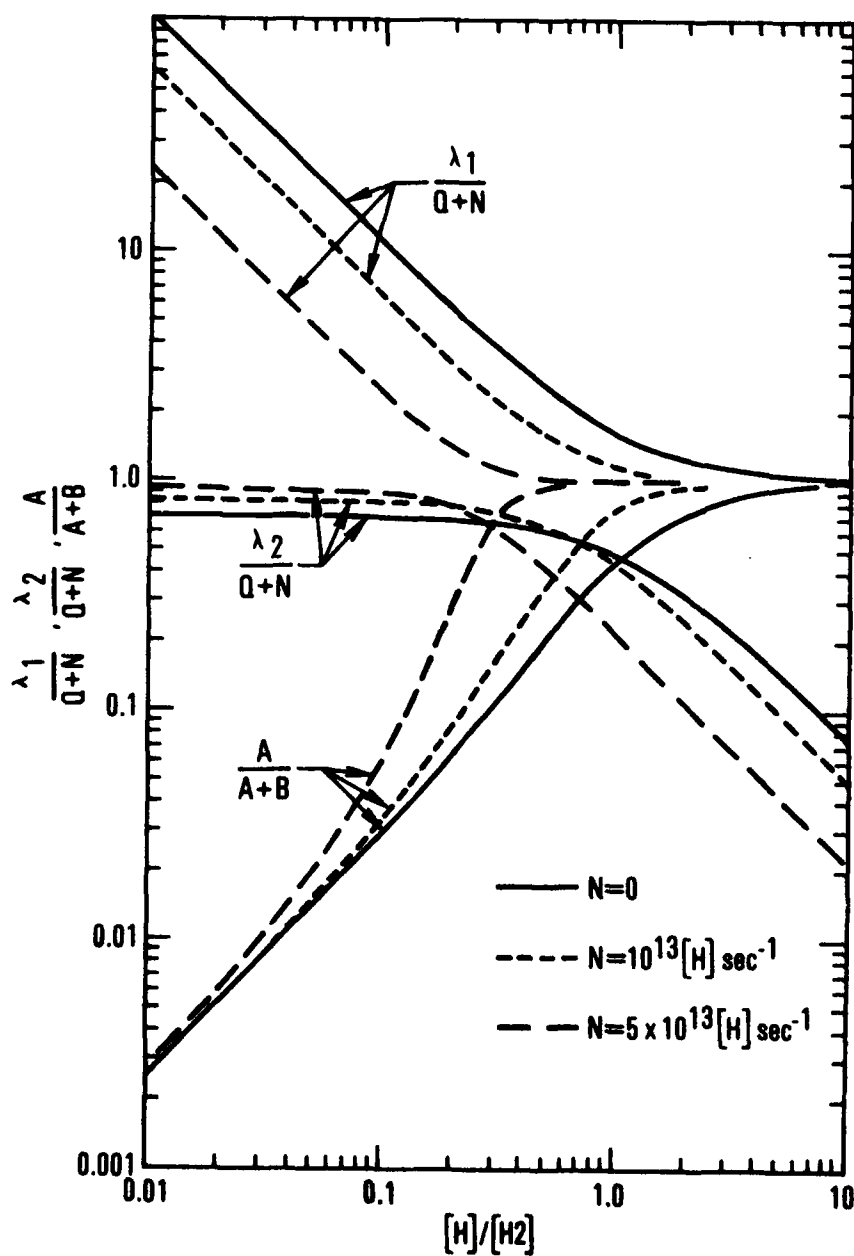$$\lambda_2 \sim \left(\frac{k_4}{k_4 + k_{-2}}\right) Q + N \tag{13}$$

Fig. 2. Solution to kinetic equations for HF(v = 3) removal (see Appendix)

where $k_4/(k_4 + k_{-2})$ has been determined[10] to be ~0.7. This decay rate is at most only 30% slower than the initial decay rate and more nearly equal to it if any substantial deactivation occurs by Reaction (3), i.e., if $k_3 \geq k_2$.

At larger H atom concentrations, $[H] \sim [H_2]$, a larger fraction of the HF(v = 3) has to dissociate before the pumping term in Equation (10), $k_{-2}\{[F][H_2]/[HF(v = 3)]\}$, becomes significant compared to the deactivation terms, $(k_2 + k_3)[H]$. Therefore, the initial decay rate, Q + N, should persist for a larger proportion of the HF(v = 3) decay. The two decay rates should be the most apparent and the most easily resolved when A ~ B in Equation (12) and when the two decay rates are quite different. For A/(A + B) = 0.5, λ_2 is only a factor of 3.3 slower than Q + N, the initial decay rate, if $k_2 \gg k_3$ (see the curve for N = 0, Fig. 2). If $k_3 \geq k_2$, there is even less of a spread between the two decay rates. The difficulty of determining whether a measured trace decays as a single exponential or as the sum of two exponentials is demonstrated in Fig. 3, where a calculated fluorescence trace described by Equation (12) is plotted with the values for λ_1, λ_2, and A/(A + B) taken from Fig. 2. The circles represent the same trace except that $0.05 \times I_o$ was subtracted to demonstrate the effect of the typical uncertainty in the baseline of such experimental data. The result is that the circles can be fitted within 2% of the full-scale reading with a single exponential decay rate. Note that the approximate fit to the circles has a decay rate within 10% of the initial decay rate of the theoretical trace. The precision of the data in these experiments is not sufficient for two
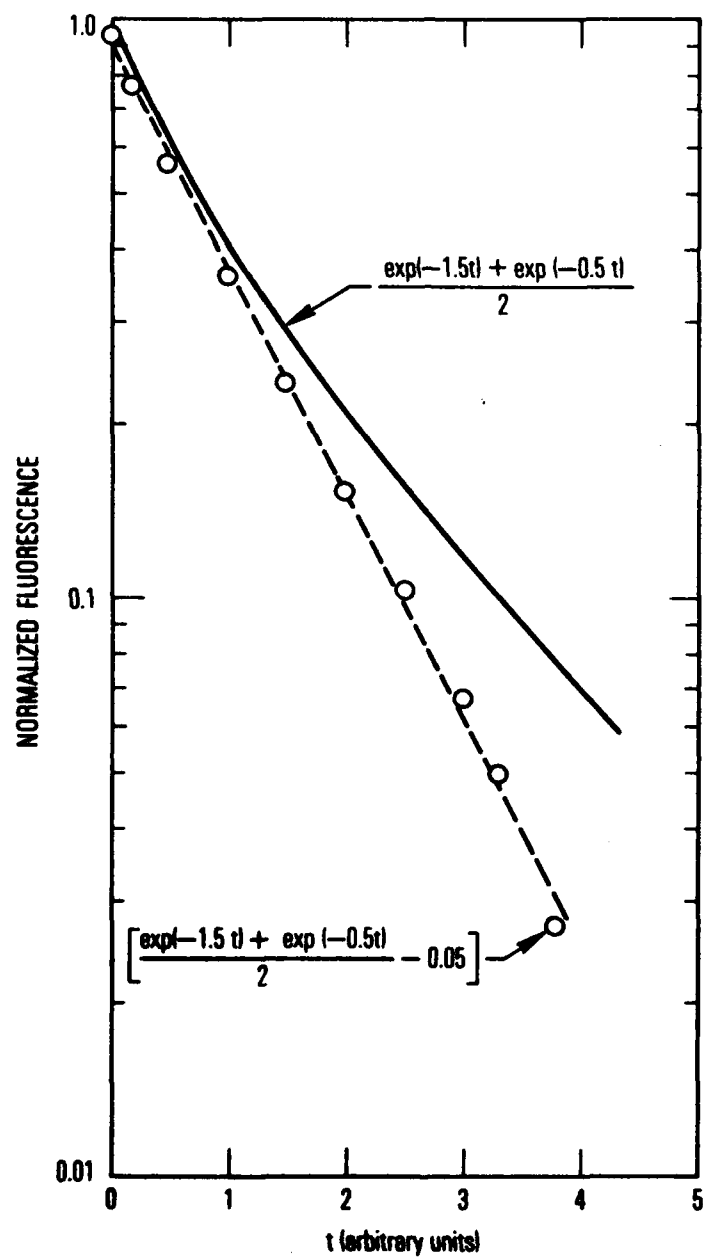
Fig. 3.   Example of double exponential
fluorescence decay

decay rates to be resolved, much less quantitatively established. The two
decay rates would be much more distinguishable if a larger fraction of the
$F + H_2$ reaction were produced in HF($v = 3$) than the currently estimated
fraction of 0. 28, i. e., if Reaction (4) were slower relative to Reaction (-2).

In the light of these uncertainties, we can only interpret the measured
values of k in Equation (1) as

$$k = A k_2 + k_3 \tag{14}$$

with A between 0. 7 and 1.

The rate coefficient for Reaction (2) has not been measured. However,
it can be estimated on the basis of the overall reaction rate for $F + H_2$, the
relative vibrational distributions, and the equilibrium constant $K_{2, -2} =$
k_2/k_{-2}. Cohen and Bott[10] reviewed the data for the $F + H_2$ reaction and
recommend a rate coefficient of

$$k_{F + H_2} = 2. 3 \times 10^{14} \exp(-1600/RT) \tag{15}$$

with a value of $(1. 5 \pm 0. 5) \times 10^{13}$ cm^3/mol-sec at 295 K. In the same
review, Cohen and Bott recommend a value of 0. 28 for the branching fraction
into the v = 3 level, i. e., $k_{-2}/(k_{-2} + k_4) = 0. 28$, or a value of $4. 2 \times 10^{12}$
cm^3/mole-sec for k_{-2}. A value of $K_{2, -2} = 3. 2$ at 295 K can be calculated
from the JANAF thermodynamic data[13] (Table V). The uncertainty in this
value stems largely from the uncertainty in the bond dissociation energy
(BDE) of HF since the exothermicity of Reaction (2) depends directly on the

Table V. JANAF Thermodynamic Data[13]

Species	ΔH_{298} kcal/mol
H	52. 100
D	53. 252
HF(v = 0)	-65. 140
HF(v = 3)	-32. 623
H_2	0.000
HD	0.076
F	18. 860

bond dissociation energies of HF and H_2 and the spectroscopically determined energy levels of HF. The exothermicity of Reaction (2) at 0 K is simply $\Delta E = BDE(H_2) - BDE(HF) + E_{HF(3)} - E_{HF(0)}$, where $E_{HF(3)} - E_{HF(0)}$ is the energy difference between HF(v = 3) and HF(v = 0). The JANAF thermodynamic data (Table V) are based upon a value[14] of 135,120 ± 300 cal/mol for BDE(HF) at 0 K. A more recent measurement by Di Lonardo and Douglas[15] gave a value of 135,274 ± 170 cal/mol, which agrees with the earlier measurement. An uncertainty of 200 cal/mol produces an uncertainty of a factor of 1.4 in the calculated value of $K_{2,-2}$ at 295 K [a larger value for BDE(HF) gives a smaller value for $K_{2,-2}$].

With the value of 3.2 for $K_{2,-2}$ and the recommended value for k_{-2}, a rate coefficient of $k_2 = 1.37 \times 10^{13}$ cm^3/mol-sec is obtained, compared to $(6.3 \pm 1.5) \times 10^{13}$ cm^3/mol-sec obtained in the experiments for the total removal rate at 295 K.[6] These two values differ by a factor of 4.6. The uncertainty of a factor of 1.5 in the overall F + H_2 rate[10] and the fraction of the reaction going into v = 3 combined with the factor of 1.4 uncertainty in $K_{2,-2}$ gives a total uncertainty of a factor of 2 in the estimated value of k_2. The estimated upper limit of 2.7×10^{13} for k_2 is a factor of 1.8 lower than our estimate of the lower limit of 4.8×10^{13} cm^3/mol-sec for the removal rate.

Although there have been no prior experimental studies of Reaction (2), Wilkins[2] has performed trajectory calculations on an LEPS potential energy surface. He obtained a value of 4.2×10^{12} cm^3/mol-sec for k_2, compared

to the value of 1.37×10^{13}, which was calculated from the equilibrium constant and the value of k_{-2} recommended by Cohen and Bott.[10] In a separate calculation,[16] $k_{-2} = 2.66 \times 10^{12}$ cm^3/mol-sec was obtained; the recommended value is 4.2×10^{12} cm^3/mol-sec. Wilkins' two calculated rates yield a value of 1.6 for $K_{2, -2}$, a factor of 2.0 lower than that calculated from the JANAF data. However, a factor of 2 is probably within the accuracy of the trajectory calculations. Wilkins' calculations suggest that k_2 may be $<10\%$ of the total measured removal rate of HF($v = 3$).

B.   TEMPERATURE DEPENDENCE OF HF($v = 3$) REMOVAL

   BY H

The temperature dependence of Reaction (2) can be estimated from existing data. Coombe and Pimentel[17] measured the temperature dependence of the fraction of the F + H_2 reaction going into $v = 3$, relative to the fraction yielding $v = 2$. They found that

$$\frac{k_{-2}}{k_4(v = 2)} = 0.39 \exp(117/RT) \tag{16}$$

Approximately 55% of the F + H_2 reactive collisions yield HF($v = 2$); therefore, the temperature dependence of $k_4(v = 2)$ can be approximated with that of the overall reaction. Combining Equations (15) and (16) produces the expression

$$k_{-2} = 4.9 \times 10^{13} \exp(-1483/RT) \tag{17}$$

The equilibrium constant determined from the JANAF data can be described between 200 and 400 K as follows:

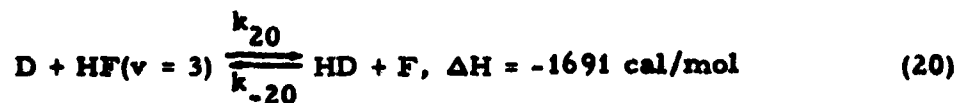$$K_{2, -2} = 0.338 \, T^{0.179} \exp(723/RT) \tag{18}$$

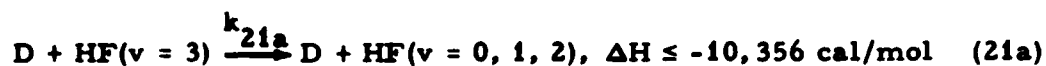Thus, an expression for k_2 can be derived from Equations (17) and (18)

$$k_2 = 1.7 \times 10^{13} \, T^{0.179} \exp(-760/RT) \tag{19}$$

Written as a simple Arrhenius expression, k_2 has an effective activation energy of 850 cal/mol, which is unlike the negative activation energy of the measured removal rate. The calculated value of k_2 at $T = 200$ K is $\sim 0.7 \times 10^{13}$ cm^3/mol-sec, roughly 7% of the measured removal rate of 10×10^{13} cm^3/mol-sec. As earlier work concluded,[6] the reaction to form H_2 + F is insufficient to explain the removal of HF($v = 3$) by H.

C.   REMOVAL OF HF($v = 3$) BY D ATOMS

The measured removal rates of HF($v = 3$) by D atoms (5.9×10^{13} cm^3/mol-sec at 295 K and 7.9×10^{13} at 200 K) were within 20% of the slightly faster rates measured for HF($v = 3$) removal by H atoms. The removal of HF($v = 3$) by D atoms can be described with the following set of reactions:

$$D + HF(v = 3) \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} HD + F, \quad \Delta H = -1691 \text{ cal/mol} \tag{20}$$

$$D + HF(v = 3) \xrightarrow{k_{21a}} D + HF(v = 0, 1, 2), \quad \Delta H \le -10,356 \text{ cal/mol} \quad (21a)$$

$$\xrightarrow{k_{21b}} H + DF \quad (21b)$$

and possibly

$$F + D_2 \longrightarrow D + DF \quad (22)$$

For the conditions of the present experiment, the concentration of HD was always small compared to that of D_2 so that Reaction (-20) can be neglected, and the HF(v = 3) can be expected to decay exponentially. The difference in the decay rates with and without the microwave discharge is simply

$$\Delta \left(\frac{1}{\tau} \right) = (k_{20} + k_{21}) [D] \quad (23)$$

where the term $-1/2 \, k_{HF(v)-D_2}$ was neglected with respect to $(k_{20} + k_{21})$. The rate of HF(v = 3) relaxation by D_2, $k_{HF(3) - D_2}$, was found in a separate study[18] to have a value of 1×10^{12} cm^3/mol-sec at 295 K.

Berry[19] determined the overall rate for HF formation by the F + HD reaction to be slower than that for F + H_2 by a factor of 2.5 at room temperature. He also determined that Reaction (-20) accounted for 10% of the overall F + HD → HF + D reaction. With Berry's results and the value of 1.5×10^{13} cm^3/mol-sec that Cohen and Bott[10] recommended for the F + H_2 rate coefficient at 295 K,

$$k_{-20} = 6.0 \times 10^{11} \text{ cm}^3/\text{mol-sec at 295 K}$$

can be calculated. The equilibrium constant $K_{20, -20}$ is 35 at 295 K according to a calculation based on the JANAF thermodynamic data (Table V). Therefore, k_{20} has a value of 2.1×10^{13} cm^3/mol-sec at 295 K, somewhat larger than the value of $k_2 = 1.37 \times 10^{13}$ for the comparable reaction for H instead of D. This value of k_{20} is ~ 2.8 smaller than the total removal rate of 5.9×10^{13} cm^3/mol-sec measured in the experiment.

The value of k_{20} is uncertain in the same proportion as k_2 since they are both derived from the value of k_{-2}. It has an additional uncertainty associated with Berry's measurements of the F + HD $\rightarrow$ HF + D reaction rate relative to that for F + H$_2$ $\rightarrow$ HF + H and the fraction going into HF(v = 3). He obtained distribution numbers for the pumping reactions only slightly different from the accepted values. [10] There have been no measurements of the temperature dependence of Reaction (20); therefore, there is no guide to the rate at 200 K. It should be mentioned that Wilkins[20] made trajectory calculations on an LEPS potential energy surface for Reaction (-20) and obtained a rate coefficient of

$$k_{-20} = 1.35 \times 10^{13} \exp(-1628/RT) \text{ cm}^3/\text{mol-sec} \qquad (24)$$

which has a value of 8.4×10^{11} cm^3/mol-sec at 295 K, compared to the value of 6.0×10^{11} cm^3/mol-sec calculated from Berry's data and the recommended rate for F + H$_2$. Equation (24) has an activation energy very close

to the exothermicity of Reaction (20). Therefore, it is inferred from Wilkins' rate for k_{-20} and the JANAF thermodynamic data that the activation energy of k_{20} is essentially zero.

D. COMPARISONS WITH OTHER DATA

The only previous experimental study of HF(3) removal by H atoms was a flow-tube study by Kwok and Wilkins.[3] However, in their experiments, there were equal parts of HF and H since the HF(v) was produced by reacting F atoms with H_2. The decay rates were measured at various H_2 concentrations and then extrapolated back to $[H_2] = 0$, where the decay rate should be the result of processes involving HF and H and spontaneous emission. Their measurements extrapolated to $[H_2] = 0$ yielded 1.8×10^{13} cm^3/mol-sec for the rate of removal of HF(3) by H and HF. This value is a factor of 3.5 slower than the present results, even though it contains the additional contribution of HF self-relaxation. On the other hand, Kwok and Wilkins deduced a much faster rate coefficient (by a factor of 20) for the deactivation of HF(v = 2) by H atoms than our measurements indicate.[6] Since the flow-tube values are slower for v = 3 and faster for v = 2, it is possible that the effects of HF-HF V-V coupling have to be taken into account. The interpretation of those flow-tube experiments is still under investigation.

Two theoretical studies[1,2] of the relaxation of HF by H atoms in Reaction (3) have been made; both were Monte Carlo classical trajectory calculations. Thompson's[1] calculations were performed at temperatures $\gtrsim 600$ K, but his results indicate that the deactivation rate increased

approximately as the vibrational level v. Wilkins calculated[2] the deactivation rates of several vibrational levels of HF by H atoms with a semi-empirical LEPS potential energy surface. The initial calculations were performed with a 1500 cal/mol barrier height for H-F-H, but his results for the v = 1 level were faster than experimental results;[3-5] therefore, the effect of barrier height was examined.[21] Calculations with barriers of 1500, 2500, and 3500 cal/mol gave deactivation rates of 2.5×10^{12}, 3.1×10^{11}, and 3.1×10^{10} cm^3/mol-sec for the first vibrational level at room temperature; the value of 3.1×10^{11} agreed with the experimental data. In each case, the deactivation rate of HF(v = 3) was ~6 times faster than that for v = 1, and the final vibrational states were approximately equally distributed over v = 0, 1, and 2, with about equal proportions of reactive and nonreactive deactivation.

Recently, an _ab initio_ calculation by Bender, Garrison, and Schaefer[7] indicated that the H-F-H surface has a barrier height of ~40 kcal/mol. Preliminary results of a similar calculation by Wadt and Winter[8,9] also indicate a high barrier of 36 ± 4 kcal/mol and differ markedly from an LEPS angular dependence. Wilkins[21] performed a trajectory calculation on an LEPS surface with a 40 kcal/mol barrier and obtained a deactivation rate of 2.5×10^{12} cm^3/mol-sec. Thus, all of the trajectory calculations gave significantly smaller values for k_3 than the values of $(k_2 + k_3)$ obtained in the present study. The calculations also exhibit positive activation energies, compared to the negative activation energy of the present measurements.

The vibrational level $v = 3$ of HF is 38.3 kcal/mol above the bottom of the well on the potential energy surface, which is comparable to the barriers to F-atom transfer estimated by Bender et al. [7] and by Wadt and Winter. [8,9] Smith and Wood [22] investigated the relaxation of vibrationally excited molecules when an atom exchange is possible. They found that vibrational excitation above the barrier not only permits atom exchange with consequent loss of vibrational energy but also allows multiple barrier crossings, which increase the possibility for conversion of vibrational energy to rotational or translational energy, regardless of whether or not reaction occurs.

V. CONCLUSIONS

The experimental results are not precise enough to make a complete allocation of the measured removal rate to the possible removal channels. If the removal rate were the result of Reaction (2), the fluorescence traces would exhibit the sum of two exponential decay terms. These decay terms are related in such a way that extremely precise data would be required to extract the separate decay rates. The present data fit, and are analyzed in terms of a single exponential decay rate $k = Ak_2 + k_3$, where $0.7 < A < 1$.

Reaction (2) contributes substantially to the measured decay rate. Accepted thermodynamic and kinetic data for the H + HF system were used to estimate $k_2/k = 0.2 \, ^{+0.2}_{-0.1}$ at 295 K. Similarly, $k_{20}/(k_{20} + k_{21}) = 0.4 \, ^{+0.4}_{-0.2}$ has been estimated for the D + HF(v = 3) deactivation at 295 K. The largest uncertainty in the thermodynamic data for Reaction (2) is in the bond dissociation energy of HF. An uncertainty of 200 cal/mol in the value produces an uncertainty of a factor of 1.4 in the calculated equilibrium constant for the reaction at 295 K.

The removal rate for HF(v = 3) by H atoms is ~ 100 times faster than that for HF(v = 2). Unless Reaction (2) represents $>95\%$ of this rate, which is highly improbable, the V → R, T deactivation of HF(v = 3) must be much faster than the V → R, T deactivation of HF(v = 2). A collision of HF(v = 3) with an H atom can easily have sufficient energy to result in the formation of H_2, and, if recent quantum mechanical calculations are correct, there may

be sufficient energy for the incoming H atom to abstract the F atom.   Even if these atom transfers do not occur, Smith and Wood[22] found greatly enhanced vibrational deactivation probabilities in theoretical studies of similar triatomic systems in which atom exchanges were energetically possible.

The T^{-1} temperature dependence observed for the rate coefficient is very similar to that observed for the relaxation of HF(v = 1)[23,24] and HCl(v = 1).[25]   Zittel and Moore[25] discussed the HCl and HBr results and their possible explanation in terms of attractive potentials, multiple encounters, long-lived bimolecular collisions, and complex formation.   These mechanisms suggest increasing vibrational relaxation rates at decreasing temperature and may apply to the deactivation of HF(v = 3) by H atoms.   The present results do not agree well with published trajectory calculations, and additional calculations made with approximations to a more realistic surface would be very useful.
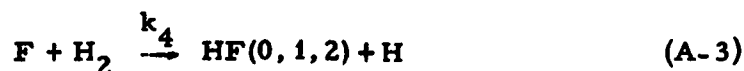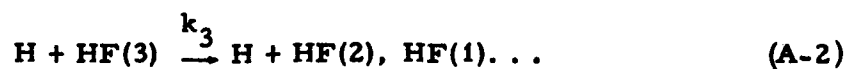
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APPENDIX

Consider the following simplified set of reactions that dominate the decay of HF(3) in the presence of H atoms:

$$H + HF(3) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + F \tag{A-1}$$

$$H + HF(3) \overset{k_3}{\longrightarrow} H + HF(2), \; HF(1) \ldots \tag{A-2}$$

$$F + H_2 \overset{k_4}{\longrightarrow} HF(0, 1, 2) + H \tag{A-3}$$

The differential equations that describe these reactions under the conditions of the present experiments are equivalent to those for the vibrational energy relaxation processes:

$$Y + X^* \rightleftharpoons X + Y^* \tag{A-4}$$

$$Y + X^* \longrightarrow Y + X \tag{A-5}$$

$$Y^* + X \longrightarrow X + Y \tag{A-6}$$

where $HF(3) = X^*$, $F = Y^*$, $H_2 = X$, and $H = Y$. When $[F] = Y^* = 0$ at $t = 0$, the solution to these two sets of equations is given by

$$X^* = [HF(3)] = A \exp(-\lambda_1 t) + B \exp(-\lambda_2 t) \tag{A-7}$$

$$Y^* = [F] = C[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \qquad \text{(A-8)}$$

The two decay times λ_1 and λ_2 can be expressed as[23]

$$\lambda_1 + \lambda_2 = Q + P + N + K \qquad \text{(A-9)}$$

$$\lambda_1 \times \lambda_2 = QK + PN + NK \qquad \text{(A-10)}$$

where $Q = k_2 [H]$, $P = k_{-2}[H_2]$, $N = k_3 [H]$, and $K = k_4 [H_2]$.

From Reactions A-1 and A-2, it is seen that

$$\frac{d(HF(3))}{dt} = - [HF(3)] (Q + N) + [F]P \qquad \text{(A-11)}$$

Equations (A-7) and (A-8) can be substituted into Equation (A-11). After collecting the terms containing $\exp(-\lambda_1 t)$ and $\exp(-\lambda_2 t)$, two equations are obtained which can be solved for $A/(A + B)$ to yield:

$$A/(A + B) = \frac{Q + N - \lambda_2}{\lambda_1 - \lambda_2} \qquad \text{(A-12)}$$

The initial exponential decay rate is always $Q + N$ since $[F]$ is initially zero in Eq. (A-11). Therefore, it is convenient to normalize λ_1 and λ_2 with $Q + N$. Calculations have been performed with the rate coefficients listed in Table IV for the conditions of $[H_2] = 3.0 \times 10^{-9}$ mol/cm^3 and various H atom concentrations. The normalized values for λ_1, λ_2, and $A/(A + B)$ have been plotted versus $[H]/[H_2]$ in Fig. 2 for three values of $N = k_3 [H]$.